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PHOSPHORUS REMOVAL PRACTICE

James F. Kreissl

Environmental Protection Agency
Cincinnati, Ohio

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J. F. Kreissl

Sanitary Engineering Institute
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ABSTRACT

PHOSPHORUS REMOVAL PRACTICE

J. F. Kreissl

Examples of available phosphorus removal processes are presented in the form of results from specific installations. Installations were chosen to illustrate specific types of phosphorus removal systems. Primary, secondary, and tertiary chemical-addition techniques are emphasized due to their higher reliability and lower costs.

PHOSPHORUS REMOVAL PRACTICE*

James F. Kreissl**

INTRODUCTION

The most discussed of the major nutrients is phosphorus. This stems from a number of factors, primarily its relative ease of removal and the fact that its major source is wastewater effluents. Traditional treatment methods have little efficacy in removing this pollutant. Typical values of removal efficiencies are illustrated in Table I[1]. Higher removals reported in the literature have been attributed to the unique character of the wastewater or chemical precipitation phenomena. Although a large number of approaches have been utilized for phosphorus removal, the discussion will be limited to processes which utilize chemical additions because of their economics and reliability.

Of the chemicals proposed for phosphorus removal the major ones have been aluminum and iron salts and lime. With any of these chemicals a polymer may be required for good solids separation. The relative value of each chemical varies due to individual circumstances. The factors which affect the choice of chemical are shown in Table II[2]. Influent phosphorus concentration is important with aluminum (Al) and iron (Fe) salts since the metal (Me) to phosphorus (P) ratio is

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*Presented at the Sanitary Engineering Institute, University of Wisconsin, March 9-10, 1971

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TABLE I

Phosphate Removal by Conventional
Waste Treatment Plants

Type of Treatment Plant	% Phosphorus Removal
Primary Sedimentation	5 - 15
Primary and Trickling Filter	20 - 30
Primary and Activated Sludge	30 - 50

TABLE II

Factors Affecting Choice of Chemicals

1. Influent Phosphorus Level
2. Effluent Discharge Standard
3. Wastewater Characteristics
4. Plant Size
5. Chemical Costs Including Transportation
6. Sludge Handling Facilities
7. Sludge Disposal Facilities
8. Other Processes Utilized

generally controlling. Effluent phosphorus level will control the dosage in most cases. Wastewater characteristics, especially alkalinity, can have a profound effect on chemical requirements. Plant size, in the case of lime, will indicate the economics of sludge recalcination. Chemical costs and availability may vary widely with geographical location. Sludge handling and disposal facilities may determine strong preferences for a particular chemical. The use of chemicals in secondary biological treatment processes (mineral addition), for example, may negate the possibility for lime use.

The systems considered in this discussion are chemical treatment of raw degritted sewage, mineral addition, and tertiary treatment for phosphorus removal. These alternative systems are depicted on the top, bottom, and middle diagrams, respectively, in Figure 1.

RAW-DEGRITTED SEWAGE

Chemical treatment for phosphorus, carbon, and solids removal is the first step in physical-chemical treatment of wastewaters. Whether followed by activated carbon as in this treatment sequence or biological treatment, the effluent from this primary step should contain low concentrations of suspended and colloidal solids, their associated organics, and phosphorus. When the biological process is activated sludge, reductions in air requirements and activated sludge wasting may possibly accrue as well as improved effluent quality[3].

Results of 10 weeks of control and 10 weeks of chemical addition to the primary at Grayling, Michigan, are shown in Table III[4]. The chemicals used were $FeCl_2$, NaOH and an anionic polymer. Overall removals

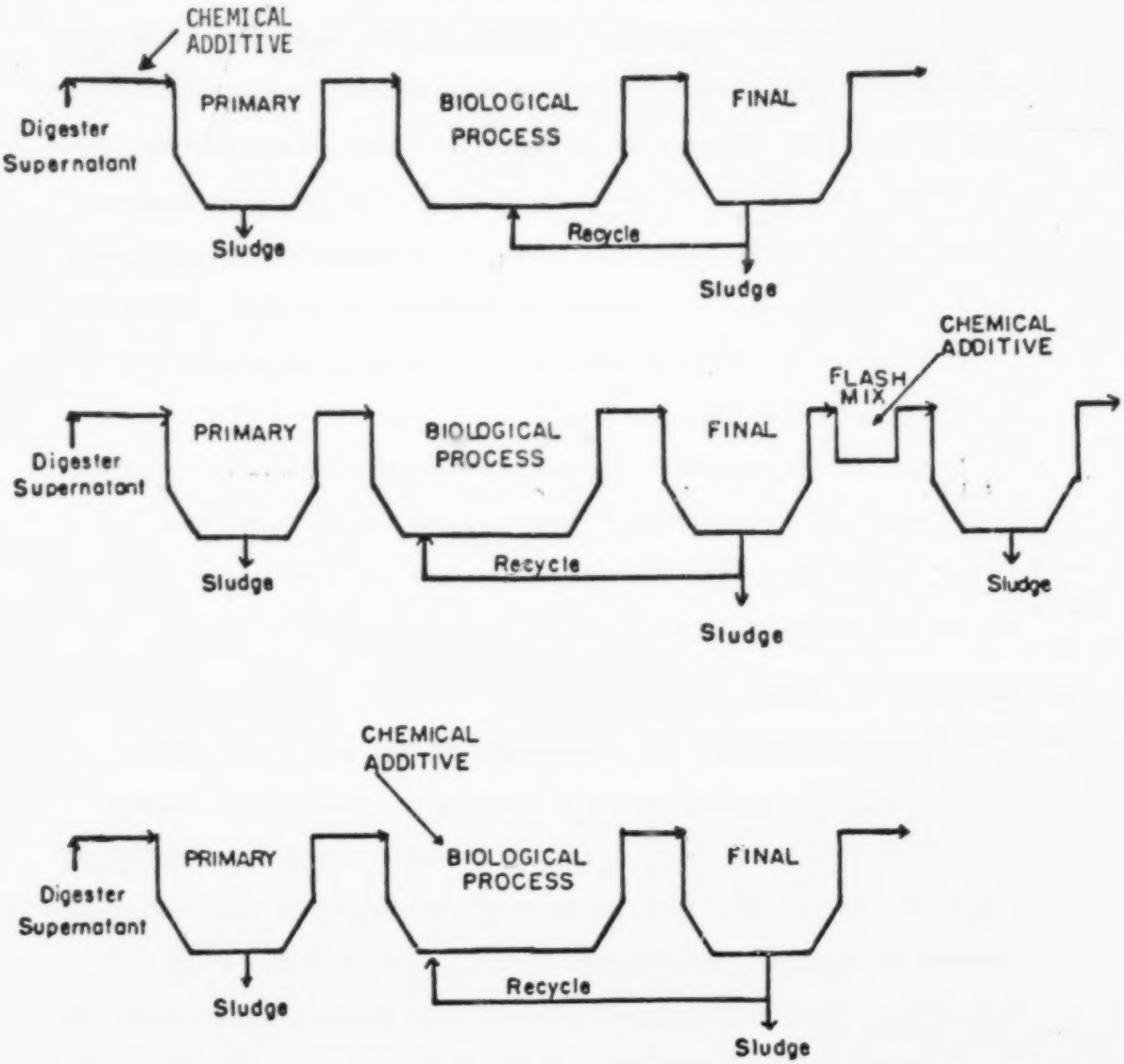


FIGURE I. PHOSPHORUS CONTROL BASIC SYSTEMS

TABLE III

Results at Grayling, Michigan

Chemicals:

$FeCl_2$ = 15 - 30 mg/l as Fe
NaOH = 30 - 50 mg/l as $CaCO_3$
A-23 = 0.3 - 0.5 mg/l

	Without Chemicals (10 weeks)			With Chemicals (10 weeks)		
	Raw mg/l	Pri. Eff. mg/l	% Rem.	Raw mg/l	Pri. Eff. mg/l	% Rem.
SS	157	78	50	224	50	78
BOD	170	101	41	178	74	58
Total P	No Removal			15.5	4.4	72

of suspended solids (SS) and biochemical oxygen demand (BOD) were increased along with 72% phosphorus (P) removal from this primary plant. X-ray diffraction of the sludge indicated that the precipitate, vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$), was the predominant form of the precipitate. Similar studies on the primary clarifier of a trickling filter plant at Lake Odessa, Michigan, produced similar improvements in overall plant removals. No problems were noted in the trickling filter or the digester during this short-term study. Digestor supernatant was found to contain only 10 to 20% of the phosphorus level found during normal operation. This would tend to indicate that phosphates are not released during anaerobic digestion.

If circumstances are favorable, the use of waste pickle liquor, as either $FeCl_2$ or $FeSO_4$, can be economically advantageous. Mentor, Ohio, used the available chloride form with lime and polymer for treatment of raw-degritted sewage. Results, shown in Table IV, indicate SS, BOD, and P removals of 74, 59, and 83.5%, respectively. Similar results were obtained with the sulfate form at Texas City, Texas[1]. It should be noted that the optimum pH for the Fe(II) - base system appears to lie at or above 8.0. Efficiency may be impaired if sufficient oxygen is not available for the oxidation of Fe(II) to Fe(III).

TABLE IV

Results at Mentor, Ohio

CHEMICALS:	
Waste Pickle Liquor ($FeCl_2$)	= 43 mg/l as Fe
Lime	= 66 mg/l
A-23	= 0.4 mg/l
PERCENT REMOVAL WITH CHEMICALS	
SS	= 74%
BOD	= 59%
Total P	= 83.5%

A short-term study of the addition of $FeCl_3$ and anionic polymer to the primary of an activated sludge plant at Benton Harbor, Michigan, showed similar results[5]. On the basis of this short-term study it was indeed noted that additional solids were generated, but the increased density of the sludges actually reduced the volume pumped with no losses in digestor operation. These results are shown in Table V. No increase

TABLE V

Plant Data at Benton Harbor Using Ferric Chloride

	No Chemical Addition	Chemical Addition	
		Recycle to Primary*	No Recycle*
Primary Clarification			
Volume Pumped, Gal/Day	53,200	51,600	46,100
Solids Concentration	3.80	4.29	4.82
Percent Volatile	64	63	60
Mixed Liquor Data			
Suspended Solids, mg/l	2500	2700	2400
Sludge Volume Index	85	78	64
Dissolved Oxygen	4.8	5.9	6.6
Air Applied, cfm	4480	4940	4710
Digester Operation			
Gas Production - ft^3	37,800	44,400	40,800
Gas Production - ft^3/lb of solids	3.48	3.82	3.67

*With and without Recycling of Waste Activated Sludge

in effluent iron concentrations were noted. Long-term effects of chemical addition to the primary on biological systems have not been determined, however. This information is presently being determined via a grant to Grand Rapids, Michigan, from the Environmental Protection Agency, Office of Research and Monitoring.

Stamburg, et al.[6], studied lime precipitation at Washington, D.C. The relationship between alkalinity, lime dose, and pH is shown in Figure 2. It is quite apparent that initial alkalinity strongly influences the lime requirement. At the same time pH is the controlling factor in phosphorus removal by lime treatment as shown in Figure 3.

FIGURE 2. ALKALINITY, LIME DOSE, AND pH.

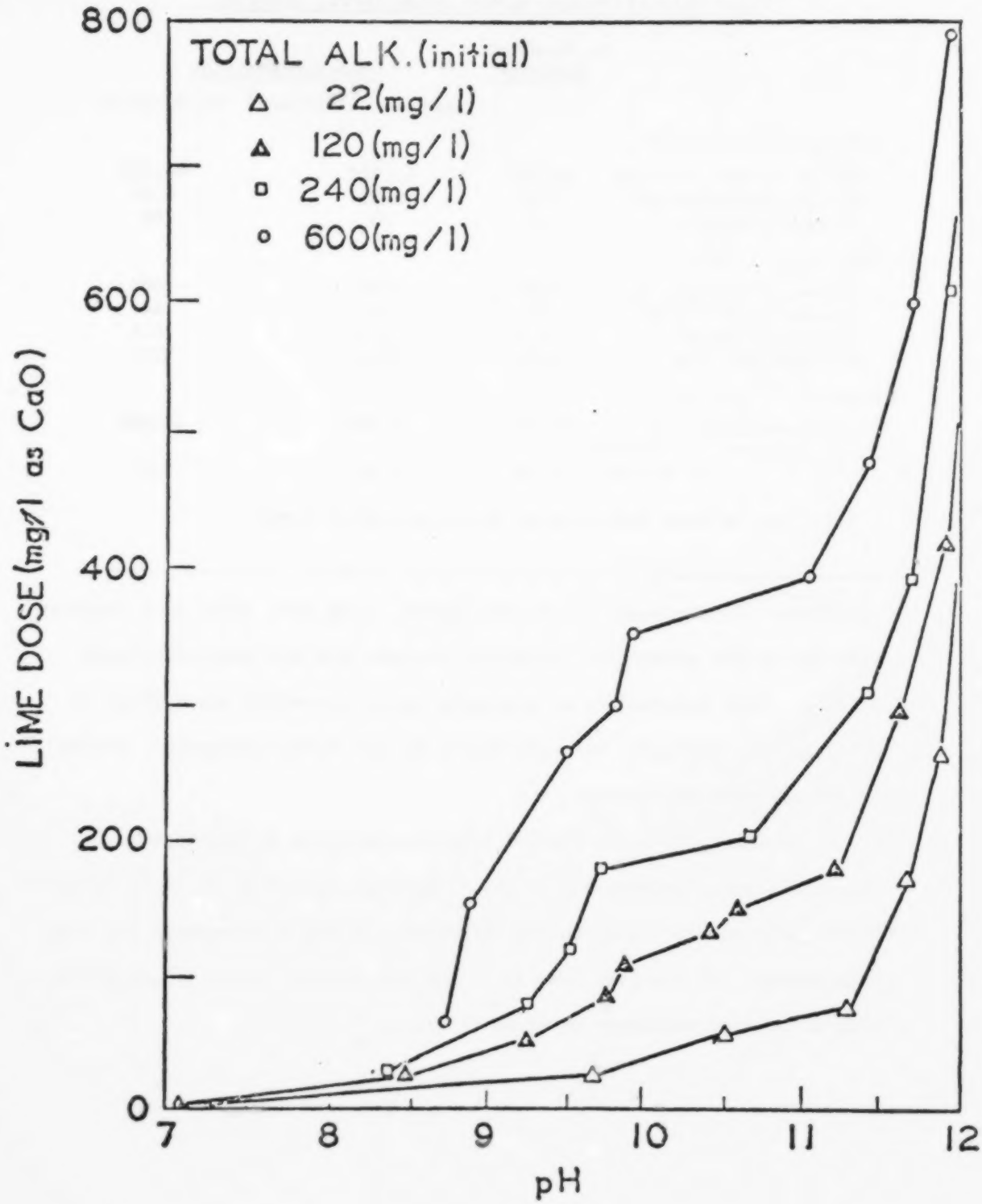
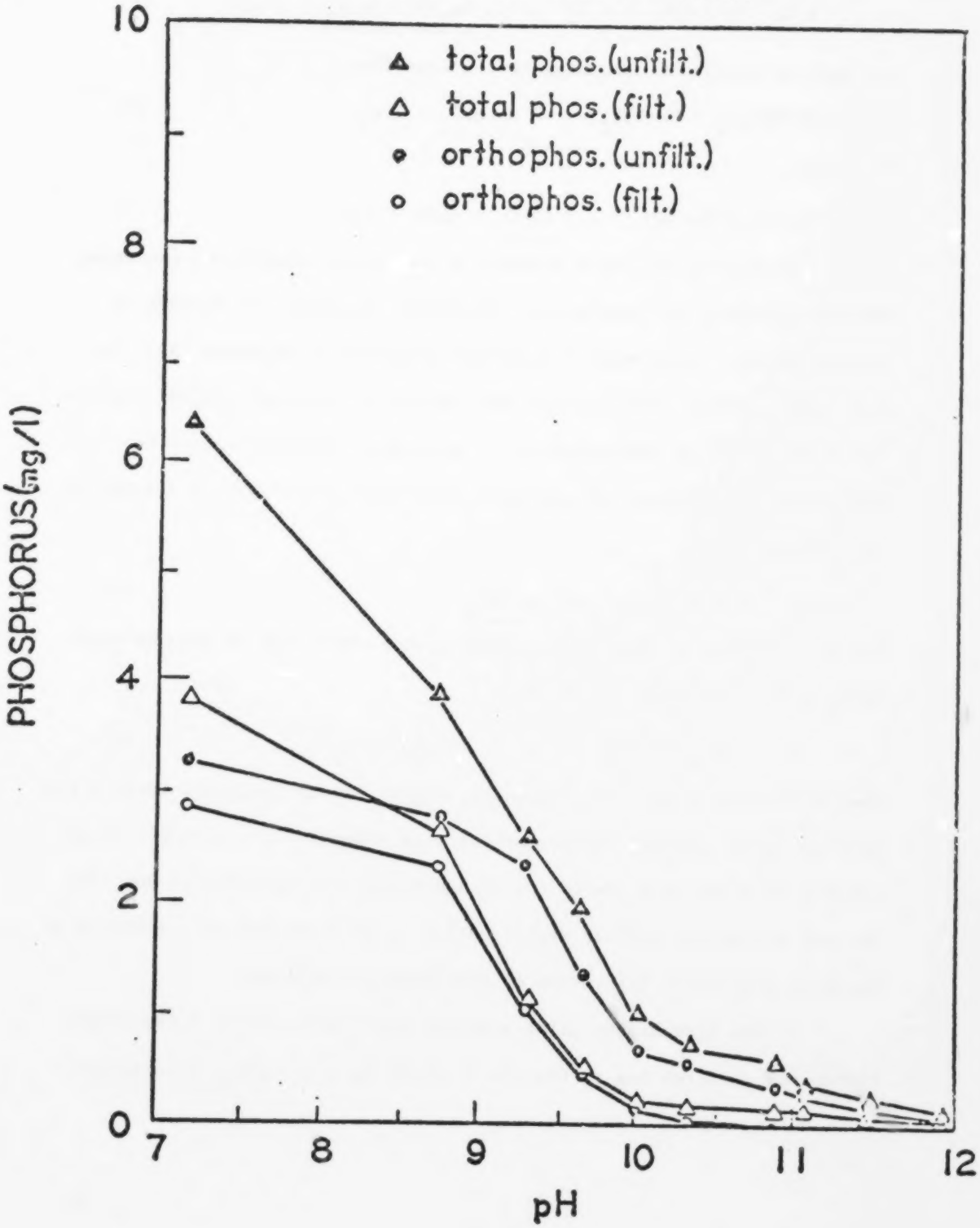


FIGURE 3.

LIME PRECIPITATION AND PHOSPHORUS REMOVAL FROM RAW WASTEWATER.



Lime addition accomplishes the precipitation of the phosphorus in the form of calcium hydroxyapatite according to the equation:

$$5\ Ca^{++} + 3\ HPO_4^{=} + 4\ OH^- \text{ ----> } \underline{Ca_5(OH)(PO_4)_3} + 3\ H_2O \qquad (1)$$

and calcium carbonate according to the equations:

$$Ca(HCO_3)_2 + Ca(OH)_2 \text{ ----> } \underline{2\ CaCO_3} + 2\ H_2O \qquad (2)$$

or

$$NaHCO_3 + Ca(OH)_2 \text{ ----> } \underline{CaCO_3} + NaOH + H_2O \qquad (3)$$

The calcium carbonate serves the additional benefit of enhancing the settleability of suspension. Therefore, equation (2) because of greater hardness represents a superior situation to equation (3). In many cases, proper clarification may require two-stage process whereby the pH is raised to approximately 11 or greater with the additional precipitation of magnesium hydroxide which aids clarification further by the equation:

$$Mg^{++} + 2\ OH^- \text{ --------> } \underline{Mg(OH)_2} \qquad (4)$$

The pH must then be reduced by recarbonation which further precipitates $CaCO_3$ according to the reaction:

$$Ca^{++} + CO_2 + 2\ OH^- \text{ ----------> } \underline{CaCO_3} + H_2O \qquad (5)$$

When sufficient alkalinity, hardness, and as yet unquantified factors are present, it is possible to accomplish good removals with a single-stage process at relatively low ($\geq$ 10) pH according to equations (1) and (2). In both processes, further stabilization by pH reduction will probably be required along with filtration of the clarifier effluent.

At the Blue Plains pilot plant at Washington, D.C., a two-stage system was required due to the low (100-200 mg/l as $CaCO_3$) alkalinity

of the raw wastewater. This study, along with those of Weber, et al.[7], and Kreissl, et al.[8], was concerned with physical-chemical treatment, i.e., the secondary stage being activated carbon. All studies yielded excellent removals of phosphorus as well as organic carbon and suspended solids. Some results reported from the 0.1 MGD, diurnal flow D.C. study are shown in Table VI[6]. These results were obtained by a first-stage pH of 11.8 after the addition of 350 to 400 mg/l of lime as CaO. Kreissl, et al.[8], utilized a commercially-available 0.02 MGD constant-flow system with alum or ferric sulfate addition at an average dosage of 300 mg/l of each. The results for both chemicals were generally identical and are shown in the Figure 4.

Costs of chemical addition for phosphorus removal in the primary clarifier are highly variable. If an existing plant is converted to P-removal, these costs will include chemicals, storage for the chemicals, feeding equipment, labor, and sludge handling costs for the additional sludge. Five to ten pounds sludge/1000 gallons have been produced by lime addition, while iron systems show a range of about 2-5 lbs/1000 gallons[9]. Lime costs may be reduced somewhat by recalcination and reuse if the plant is of sufficient size.

MINERAL ADDITION

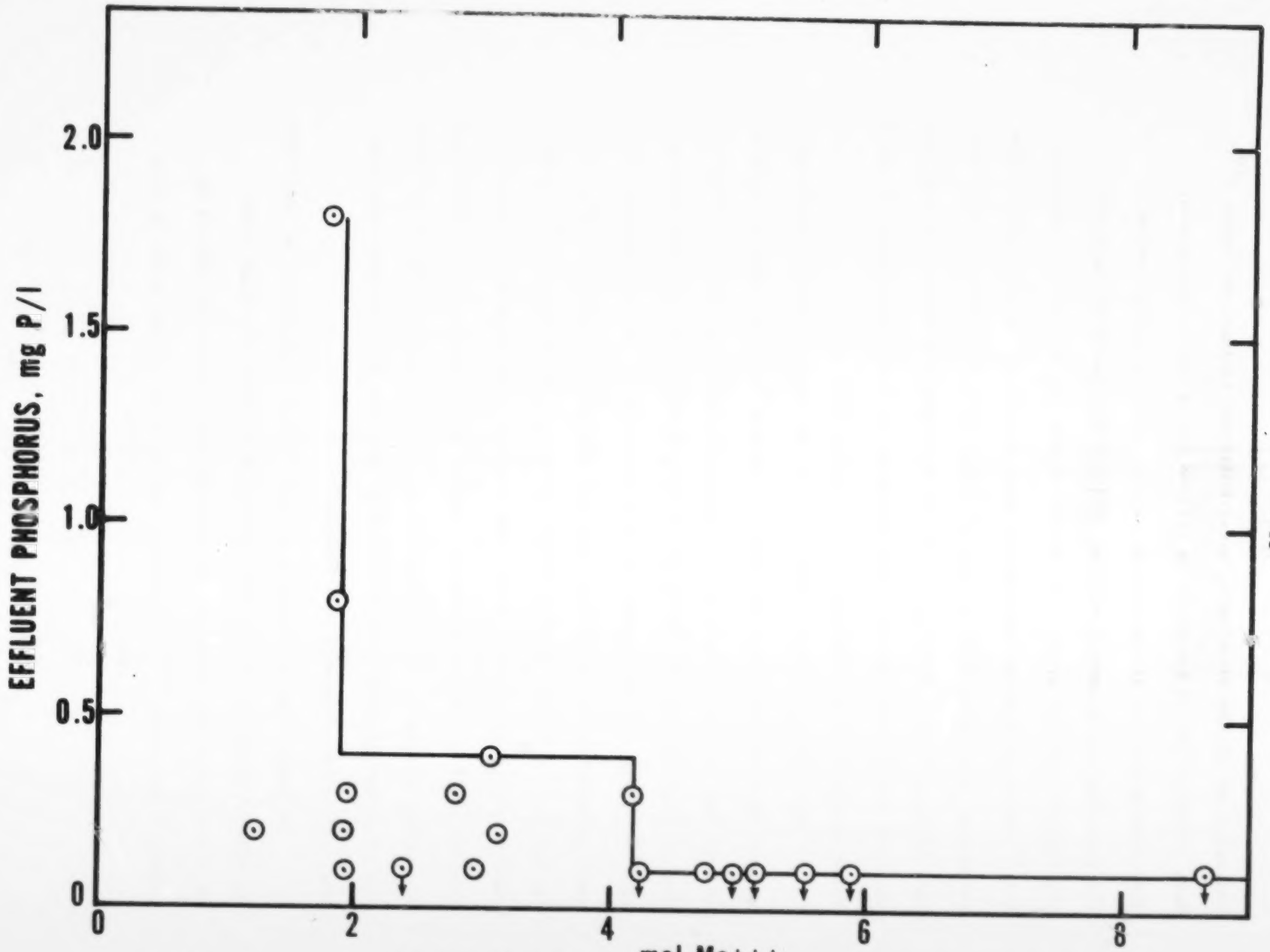
The addition of metal salts to the aeration system for phosphorus precipitation and improved mixed-liquor settling has been advocated for a number of years. The biological and chemical mechanisms involved in this process are under investigation. A Pomona, California, study readily

TABLE VI

JOINT FWQA-D.C. PILOT PLANT
PHYSICAL-CHEMICAL TREATMENT OF RAW SEWAGE

REMOVAL EFFICIENCIES

EFFLUENT	BOD		COD		SS		$PO_4^{\equiv}$	
	mg/l	% Rem	mg/l	% Rem	mg/l	% Rem	mg/l	% Rem
RAW	158	---	299	---	164	---	27.2	---
CLARIFIED	26.1	83	52.5	82.5	12	92.5	0.76	97.3
FILTERED	19.4	87.5	45.2	84.7	5.1	96.7	0.47	98.2



FUGYRE 4

RESIDUAL PHOSPHORUS vs. COAGULANT DOSE

indicates one of the advantages, i.e., coagulant savings, in Figure 5[10]. More efficient use of the metal is believed to be due to the natural flocculating ability of the biomass in the activated sludge system. The purported advantages of mineral addition are listed in Table VII. The mineral addition process has rarely caused any problems in operation. Culp[11] reported damaging buildups of inert solids in the activated sludge process at Lake Tahoe with the use of alum. This incident occurred years ago before present technology was fully developed, but serves to emphasize the need for piloting any of these processes as their performance is quite variable for different wastewaters and conditions.

The 2 MGD activated sludge plant at Pomona, California, evaluated mineral addition with alum and sodium aluminate[10]. Alum appeared to have an edge due to the presence of sufficient alkalinity in that wastewater. Sodium aluminate has the advantage in many cases due to the fact that it does not require large amounts of alkalinity for proper performance. A small-scale study at AWTRL with alum and aluminate showed the latter to be superior, illustrating the unique nature of each wastewater[12]. These results are shown in Table VIII. One problem found in mineral addition studies has been the difference of optimum pH values for the chemical and biological systems. This problem has caused some degradation in effluent turbidity despite good removals of other pollutants. Polymers have been employed to help minimize this problem.

Although some questions have been raised concerning iron compounds in mineral addition, little substantiating evidence has been found. Ferric chloride and sulfate have been used with excellent results by Thomas[13] and others[14]. Preliminary results from a grant with the City

FIGURE 5

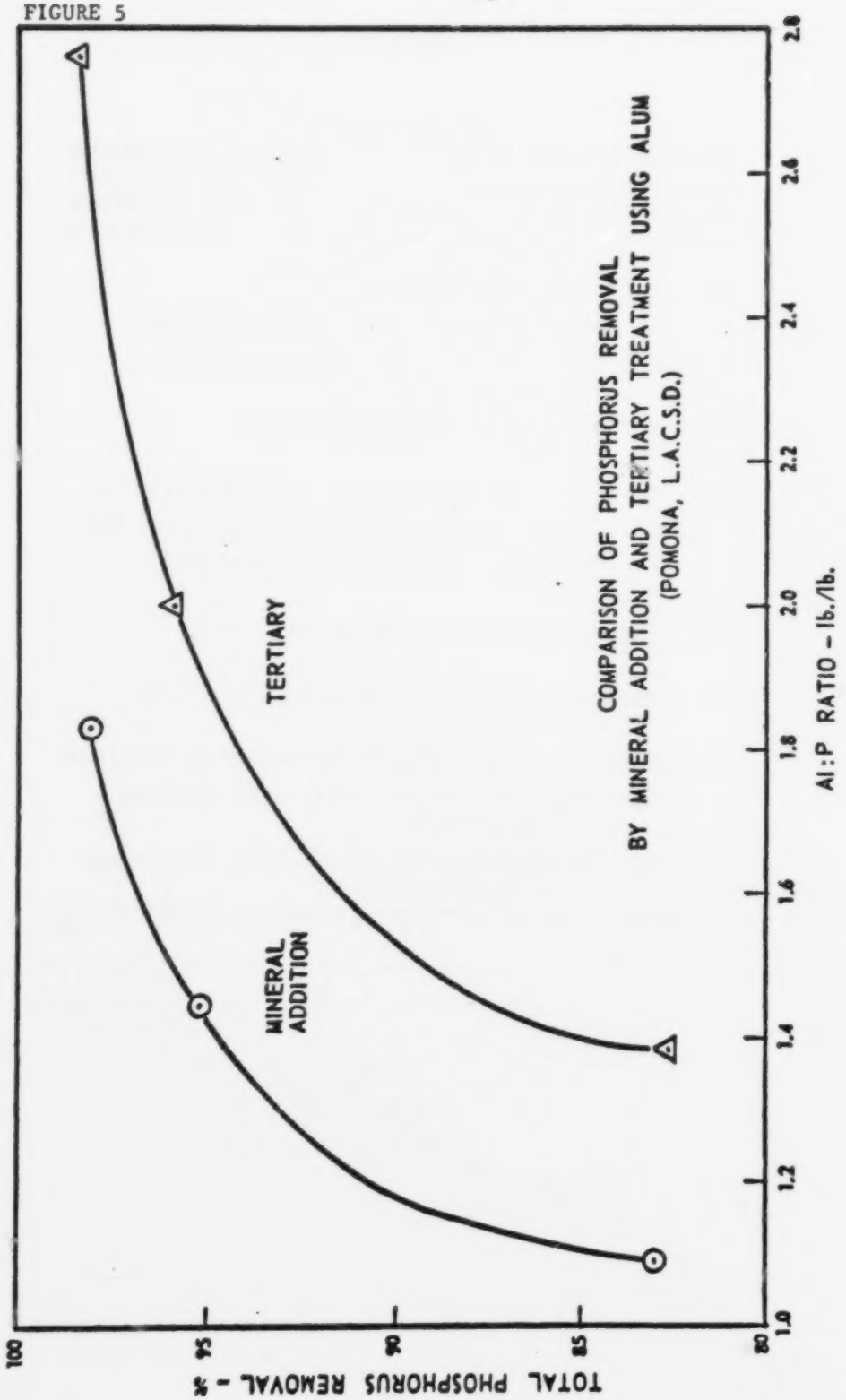

COMPARISON OF PHOSPHORUS REMOVAL
BY MINERAL ADDITION AND TERTIARY TREATMENT USING ALUM
(POMONA, L.A.C.S.D.)
TERTIARY
MINERAL ADDITION
TOTAL PHOSPHORUS REMOVAL - %
100
95
90
85
80
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
Al:P RATIO - lb./lb.

TABLE VII

ADVANTAGES OF
COMBINED BIOLOGICAL AND CHEMICAL PROCESSES

Add Mineral Supplement Directly to Aerator
1. Dual Use of Aerator
a) Mixing by Diffusion Apparatus
b) Residence Time for Reactions
2. Uses Existing Final Settler
3. Large Surface Area of Floc Available
a) Biological - Chemical Interaction
b) Reduces Chemical Requirement
4. Improves Mixed Liquor Settling
5. Reduces Effective Organic Loading
6. Reduces Supernatant Phosphorus Recycle
a) Phosphorus not Released during Digestion
b) Phosphorus Removed from Plant in Digested Sludge

TABLE VIII

COMPARISON OF ALUM DOSED AND
ALUMINATE DOSED ACTIVATED SLUDGE UNITS

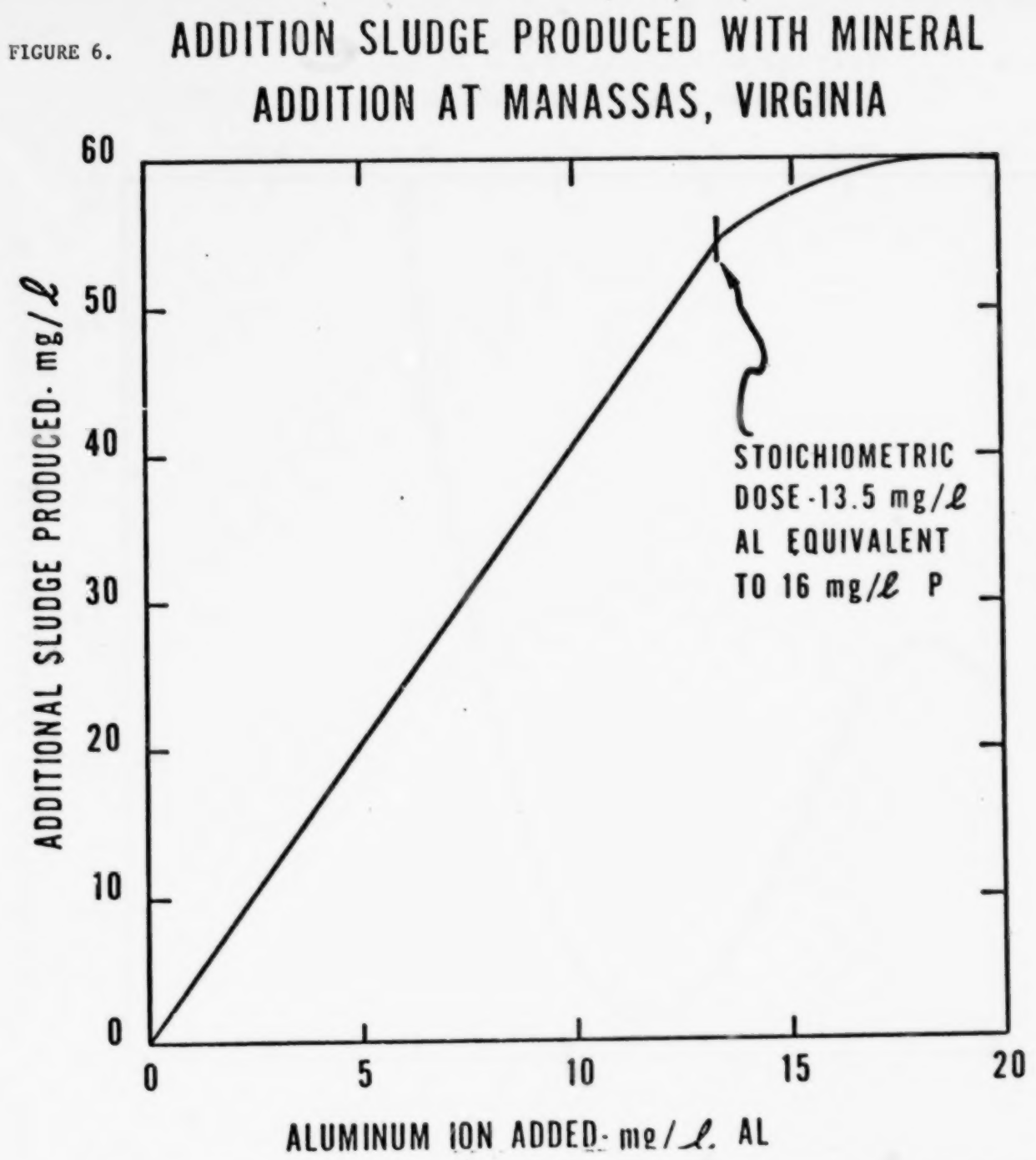
CONSTITUENT	RAW SEWAGE mg/l	FINAL EFF - ALUMINATE DOSED UNIT		FINAL EFF - ALUM DOSED UNIT	
		mg/l	% REMOVAL	mg/l	% REMOVAL
COD	310	23	93	35	89
TOTAL PHOS.	11.6	1.2	90	2.0	83
NITROGEN (ALL FORMS)	23.0	9.4	59	10.7	53
SUSPENDED SOLIDS	157	7	96	21	87
TURBIDITY - PRI EFF - (JTU)	46	3.1	93	7.4	85
ALKALINITY (as $CaCO_3$)	182	165		67	
pH	7.2	7.6		6.9	

of Milwaukee using pickle liquor ($FeSO_4$) in the aerator have been excellent[15]. Effluent phosphorus has generally been below 0.5 mg/l as P except during periods of solids loss.

An extremely short (4 weeks) study of direct dosing of trickling filters with sodium aluminate proved to be less effective than activated sludge dosing[16]. Although the dosed filter and anaerobic digestor showed no significant impairment during this study, the extremely short duration of the experiment was insufficient to properly determine any long-term effects. A cooperative study with the City of Richardson, Texas, is underway to help determine the best use of chemicals for trickling filter plants. It is felt that optimum P removal involves chemical addition either to the head of the final clarifier or split-feeding, i.e., a small percent of the total dosage to the raw waste and the remainder to the final clarifier.

Sludge volume increases have been determined at Manassas, Virginia[12]. Excess sludge production by weight is shown in Figure 6 to be about 4 lb/lb of Al(III) addition up to the stoichiometric requirement dictated by the phosphorus concentration of the wastewater. Other studies have shown higher values[12]. Actual chemical doses will vary with the wastewater characteristics, but the small-scale study of alum and sodium aluminate at AWTRL produced the pattern shown in Figure 7[12]. These two factors, increased sludge production and chemical dose requirements, are the primary determinants of the cost of the mineral addition process. As before, the cost of chemical storage and feeding as well as labor requirements will necessarily have to be considered. Table IX illustrates a cost estimate for P removal by mineral addition[21].

FIGURE 6.


ADDITION SLUDGE PRODUCED WITH MINERAL ADDITION AT MANASSAS, VIRGINIA
ADDITIONAL SLUDGE PRODUCED- mg/ℓ
60
50
40
30
20
10
0
0
5
10
15
20
ALUMINUM ION ADDED- mg/ℓ AL
STOICHIOMETRIC DOSE-13.5 mg/ℓ AL EQUIVALENT TO 16 mg/ℓ P

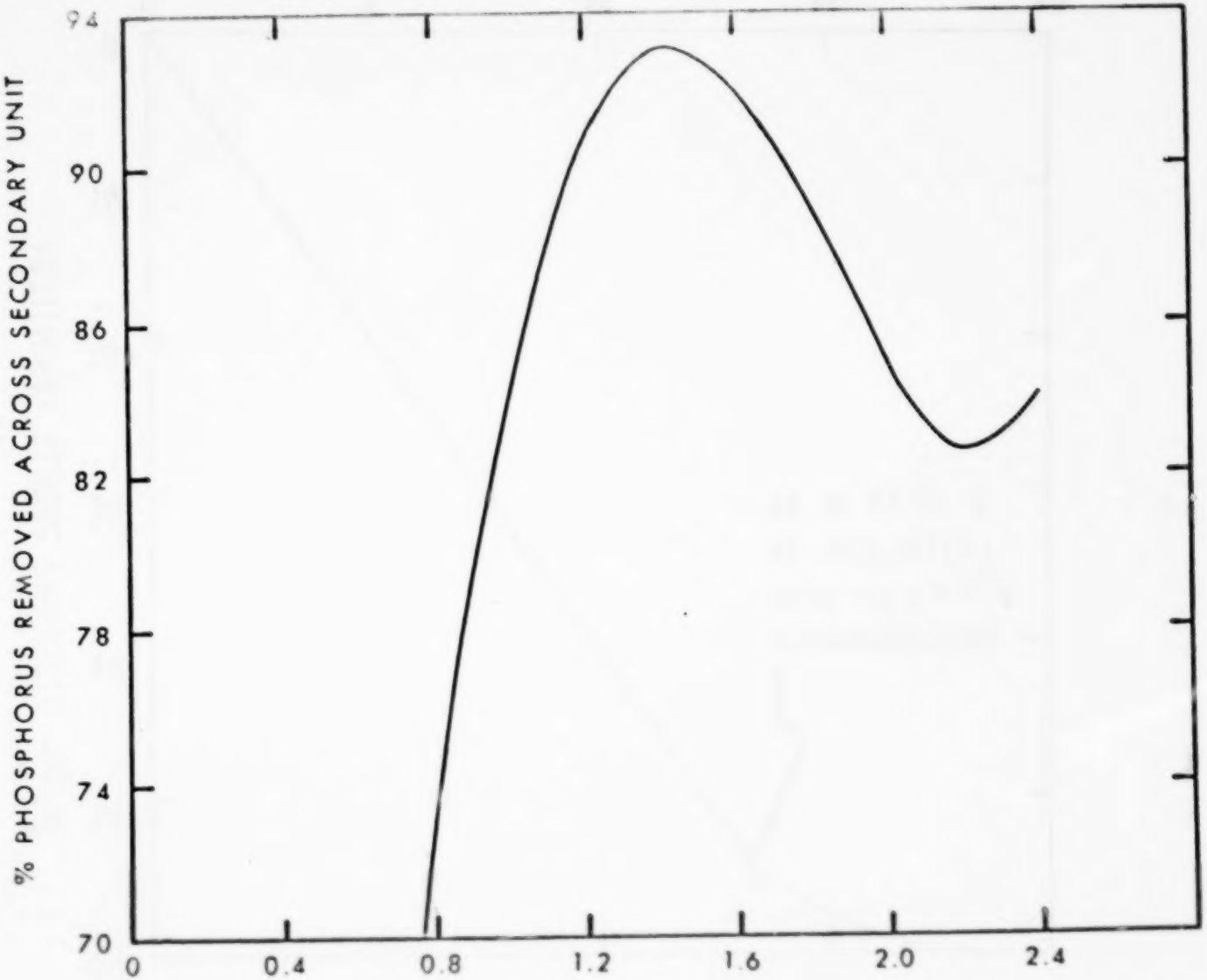

% PHOSPHORUS REMOVED ACROSS SECONDARY UNIT
94
90
86
82
78
74
70
0
0.4
0.8
1.2
1.6
2.0
2.4
ALUMINUM ION APPLICATION RATE
(lb Al +++ ADDED lb P IN PRI EFF.)

FIGURE 7.

TABLE IX

TOTAL TREATMENT COSTS

ACTIVATED SLUDGE TREATMENT

PLUS PHOSPHORUS REMOVAL

COSTS IN CENTS PER 1000 GAL. TREATED (DEC. 1970)

	PLANT SIZE - MGD		
	1	10	100
CURRENT ANNUAL OPERATING COSTS FOR CARBON AND SOLIDS REMOVAL INCLUDING DEBT RETIREMENT	33.0	10.2	5.5
CHEMICAL COST FOR 90% PHOSPHORUS REMOVAL USING ALUM (EST.) - INFLUENT PHOSPHORUS ≈ 10 mg/l P PLUS ADDITIONAL DEBT RETIREMENT AND O & M COSTS FOR PHOS. REMOVAL (ESTIMATED)	11.8	5.8	5.2
TOTAL ANNUAL OPERATING COSTS FOR CARBON, SOLIDS AND PHOSPHORUS REMOVAL (ESTIMATED)	44.8	16.0	10.7
% INCREASE IN TREATMENT COSTS FOR PHOSPHORUS REMOVAL (ESTIMATED)	36	57	95

TERTIARY TREATMENT

If a consistent, high quality effluent is desired, tertiary treatment is usually required. The first stage of tertiary treatment is generally a chemical step to remove solids and phosphorus. Four installations have reported results with this type of treatment. They are Lake Tahoe, Washington, D.C., Nassau County, New York and Lebanon, Ohio.

Blue Plains (D.C.) has tried single and two-stage treatment with lime; the latter being most successful[17]. The second stage utilized a further addition of 6 to 12 mg/l of Fe(III) to aid clarification. The results indicate that after filtration the removal of phosphorus and TOC was about 95% from the secondary effluent. Lime doses were reduced from raw waste requirements due to alkalinity reduction during secondary treatment.

The Lebanon facility used alum and lime to evaluate both chemicals for tertiary treatment. Results of alum treatment were suspended solids, phosphorus, and turbidity reductions of greater than 90%[1]. Due to the highly mineralized nature of the Lebanon wastewater, single-stage treatment with lime to a pH of 9.5 yielded excellent results in terms of clarity with filtration[18]. At this moderate pH, however, phosphorus residuals were approximately 0.5 mg/l as P, while increasing the pH slightly produced extremely low phosphorus concentrati ns. This relationship is depicted in Figure 8.

Nassau County, New York, uses alum for phosphorus removal from

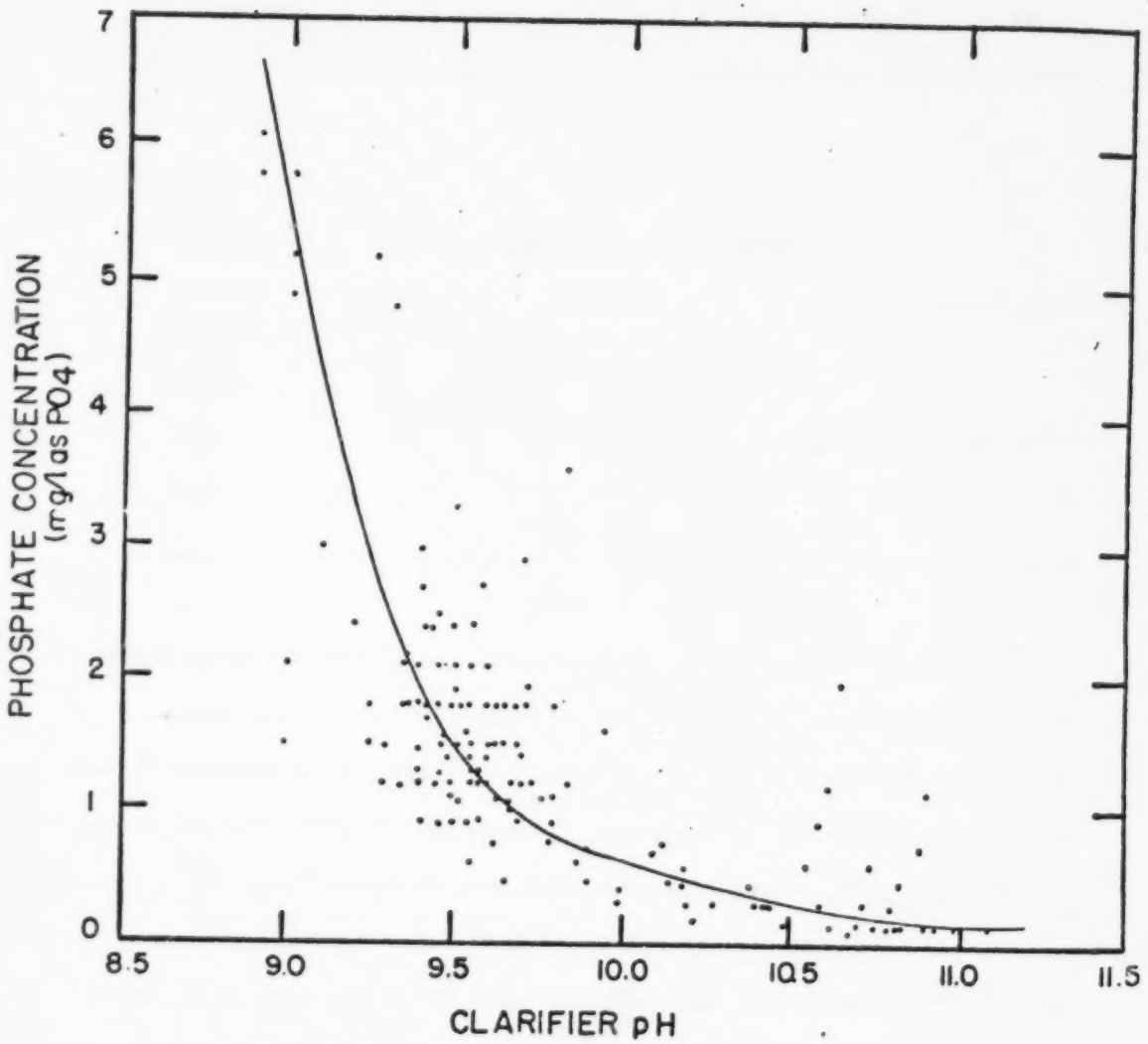


FIGURE 8. EFFECT OF pH ON PHOSPHATE CONCENTRATION OF EFFLUENT FROM FILTERS FOLLOWING LIME CLARIFIER

activated sludge secondary effluent. A 400 gpm pilot plant produced excellent P removal through the clarification steps as shown in Table X along with turbidity values[9]. This plant, like any tertiary facility, is influenced by the quality of the secondary effluent. Good quality secondary effluent is easily treatable, while upset periods will generally require adjustments.

TABLE X

Nassau County Operating Results

Constituent	Influent	Clarifier Effluent	Filter Effluent
Total Phosphate, mg/l P	7.2	1.4	0.08
Turbidity, JTU	50	6	0.2

The most famous tertiary facility is located at the South Tahoe Public Utility District. Two-stage lime clarification with ammonia-stripping of activated sludge effluent is followed by multimedia filters, activated carbon, and chlorination. The median effluent concentrations for February 1969, through January 1970, are shown in Table XI[19].

Costs for tertiary treatment at Lake Tahoe facility have been computed[19]. These costs are shown in Table XII along with total costs for the complete system. Other national average costs for unit processes involved in lime systems are estimated in Table XIII[20].

TABLE XI

Tahoe Effluent

Parameter	% of Time		
	50	80	100
BOD, mg/l	0.8	1.3	2.9
COD, mg/l	8.1	11.4	16.9
SS, mg/l	0	0	0
Turbidity, JU	0.3	0.6	1.2
P, mg/l	0.14	0.27	0.61

REF: Evans & Wilson

TABLE XII

Tahoe Costs

(¢/1000 Gal.)

Total Cost	39.6
Tertiary Cost	21.2
P-Removal:	
2-Stage Lime	4.1
Sludge Handling	5.2
Recarbonation	0.8
Filtration	4.1
Total (P)	14.2

REF: Evans & Wilson

TABLE XIII

Cost of Lime Treatment

Type of Treatment	Cost (¢/1000 gal)		
	Plant Size (mgd)		
	1.0	10	100
Single Stage Without Filtration	17	7	4
Two Stage Without Filtration	21	8	5
Filtration	7	3	1.5

Assumptions:

Upflow clarifiers and dual-media filters
Equipment amortized over 25 years at 4-1/2% interest
Settler overflow rate - 1,000 gpd/ft^2
Lime dose - 350 mg/l as $Ca(OH)_2$
Lime cost - $18.50/ton of CaO
Cost of dewatering sludge and calcining - $18.50/ton of CaO produced

SUMMARY

Although a number of P-removal systems have been cited, many have been ignored in this discussion. Consequently, a wide variety of methods are available. Many are not fully developed, but consulting engineers have sufficient options to exercise their best judgments for their clients. Each wastewater has its own specific set of conditions which may require solutions quite different from the ones cited herein.

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